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(54) Title: PROCESS OF MAKING ABSORBENT STRUCTURES COMPRISING ABSORBENT POLYMER COMPOSITIONS WITH A PERMEABILITY MAINTENANCE AGENT

(57) Abstract: A process of making an absorbent structure comprising the steps of providing absorbent polymer particles, mixing said absorbent polymer particles with a Permeability Maintenance Agent to form a blend, and further providing a carrier selected such as fibers, porous substrates like fibrous webs or foams. Further, the process includes a means for combining said absorbent polymer particle/Permeability Maintenance Agent blend with said carrier means, wherein the absorbent polymer particle/Permeability Maintenance Agent blend is combined with the carrier to form an absorbent structure, whereby a mechanical stress is exerted on said absorbent polymer particle/Permeability Maintenance Agent blend. The process includes a step for mixing the absorbent polymer particles with said Permeability Maintenance Agent prior to the combining step, whereby the SFC value of the absorbent polymer particle/Permeability Maintenance Agent blend is reduced less than that of the absorbent polymer particles without Permeability Maintenance Agent, upon being subjected to said mechanical stress.

Process of making absorbent structures comprising absorbent polymer compositions with a Permeability Maintenance Agent

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TECHNICAL FIELD

10 This application relates to a process of making absorbent structures containing absorbent particles, wherein the relatively high permeability of absorbent polymer compositions can be maintained even after mechanical stress has been applied to the polymer particles, as typically occurs during the manufacture of disposable absorbent articles. This process involves addition of a permeability maintenance agent, such as
15 fine powder(s) to the absorbent polymer compositions. This process is particularly useful for the manufacture absorbent structures for being used to absorb body fluids such as urine and menses.

BACKGROUND OF THE INVENTION

20 The development of highly absorbent articles for use as disposable diapers, adult incontinence pads and briefs, and catamenial products such as sanitary napkins, is the subject of substantial commercial interest. A highly desired characteristic for such products is thinness. For example, thinner diapers are less bulky to wear, fit better under clothing, and are less noticeable. They are also more compact in the package, making the diapers easier for the consumer to carry and store. Compactness in packaging also
25 results in reduced distribution costs for the manufacturer and distributor, including less shelf space required in the store per diaper unit.

The ability to provide thinner absorbent articles such as diapers has been contingent on the ability to develop relatively thin absorbent cores or members that can acquire and store large quantities of discharged body fluids, in particular urine. In this
30 regard, certain absorbent polymers often referred to as "hydrogels", "superabsorbents", "xerogels" or "hydrocolloids" have been particularly important. See for example, U.S. Patent 3,699,103 (Harper et al.), issued June 13, 1972, and U.S.

Patent 3,770,731 (Harmon), issued June 20, 1972, that disclose the use of such materials (hereinafter referred to as "absorbent polymers" and/or "absorbent polymer particles") in absorbent articles. Indeed, the development of thinner diapers has been the direct consequence of thinner absorbent cores that take advantage of the ability of these absorbent polymers to absorb large quantities of discharged body fluids, typically when used in combination with a fibrous matrix. See for example, U.S. Patent 4,673,402 (Weisman et al.), issued June 16, 1987 and U.S. Patent 4,935,022 (Lash et al.), issued June 19, 1990, that disclose dual-layer core structures comprising a fibrous matrix and absorbent polymers useful in fashioning thin, compact, nonbulky diapers.

These absorbent polymers are often made by initially polymerizing unsaturated carboxylic acids or derivatives thereof, such as acrylic acid, alkali metal (e.g., sodium and/or potassium) or ammonium salts of acrylic acid, alkyl acrylates, and the like in the presence of relatively small amounts of di- or poly-functional monomers such as N,N'-methylenebisacrylamide, trimethylolpropane triacrylate, ethylene glycol di(meth)acrylate, or triallylamine. The di- or poly-functional monomer materials serve to lightly cross-link the polymer chains thereby rendering them water-insoluble, yet water-swallowable. These lightly crosslinked absorbent polymers contain a multiplicity of carboxyl groups attached to the polymer backbone. These carboxyl groups generate an osmotic driving force for the absorption of body fluids by the crosslinked polymer network. Absorbent polymers can also be made by polymerizing unsaturated amines or derivatives thereof in the presence of relatively small amounts of di- or poly-functional monomers, in an analogous fashion.

The degree of cross-linking of these absorbent polymers is an important factor in establishing their absorbent capacity and gel strength. Absorbent polymers useful as absorbents in absorbent members and articles such as disposable diapers need to have adequately high sorption capacity, as well as adequately high gel strength. Sorption capacity needs to be sufficiently high to enable the absorbent polymer to absorb significant amounts of the aqueous body fluids encountered during use of the absorbent article. Gel strength relates to the tendency of the swollen polymer particles to deform under an applied stress, and needs to be such that the particles do not deform and fill the capillary void spaces in the absorbent member or article to an unacceptable degree, thereby inhibiting the rate of fluid uptake or the fluid distribution by the member or article. In general, the permeability of a zone or layer comprising swollen absorbent polymer can be increased by increasing the crosslink density of the polymer gel, thereby increasing the gel strength. However, this typically also reduces the absorbent capacity of the gel

undesirably. See, for example, U.S. Patent 4,654,039 (Brandt et al.), issued March 31, 1987 (reissued April 19, 1988 as U.S. Reissue Patent 32,649) and U.S. Patent 4,834,735 (Alemany et al.), issued May 30, 1989.

Many absorbent polymers can exhibit gel blocking under certain conditions. "Gel blocking" occurs when particles of the absorbent polymer deform so as to fill the capillary void spaces in the absorbent member or article to an unacceptable degree, thereby inhibiting the rate of fluid uptake or the distribution of fluid by the member/article. Once gel-blocking occurs, further fluid uptake or distribution takes place via a very slow diffusion process. In practical terms, this means that gel-blocking can substantially impede the distribution of fluids to relatively dry zones or regions in the absorbent member or article. Leakage from the absorbent article can take place well before the particles of absorbent polymer in the absorbent article are fully saturated or before the fluid can diffuse or wick past the "blocking" particles into the rest of the absorbent article. See U.S. Patent 4,834,735 (Alemany et al), issued May 30, 1989

This gel blocking phenomenon has typically necessitated the use of a fibrous matrix in which are dispersed the particles of absorbent polymer. This fibrous matrix keeps the particles of absorbent polymer separated from one another and provides a capillary structure that allows fluid to reach the absorbent polymer located in regions remote from the initial fluid discharge point. See U.S. Patent 4,834,735 (Alemany et al), issued May 30, 1989. However, dispersing the absorbent polymer in a fibrous matrix at relatively low concentrations in order to minimize or avoid gel blocking can significantly increase the bulkiness of the absorbent article or lower the overall fluid storage capacity of thinner absorbent structures. Using low concentrations of absorbent polymers limits somewhat the real advantage of these materials, i.e. their ability to absorb and retain large quantities of body fluids per given volume.

At relatively high concentrations, an important property of these absorbent polymers is their permeability/flow conductivity. The permeability/flow conductivity of a material can be defined in terms of its Saline Flow Conductivity (SFC). SFC is a measure of the ability of a material to transport saline fluids, such as the ability of a layer comprising swollen absorbent polymer to transport body fluids.

Typically, an air-laid web of pulp fibers (e.g., having a density of 0.15 g/cc) will exhibit an SFC value of about $200 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

Absorbent polymers with relatively high permeabilities (SFC values) can be made by increasing the level of crosslinking which increases the strength of the swollen gel, but this typically also reduces the absorbent capacity of the gel undesirably, as described

above. Surface crosslinking of absorbent polymer particles is often employed to increase the surface modulus of the particle in the swollen state, while maintaining a relatively high sorption capacity. A surface crosslinked particle has a "core-shell" structure with an exterior shell that has a higher crosslink density than the interior core of the particle. The interior of the core-shell particle typically has a lower crosslink density, and the shell typically has a higher crosslink density than a homogeneously crosslinked particle with the same capacity. Absorbent polymer compositions comprised of surface-crosslinked particles are typically more permeable to fluid in the swollen state than analogous homogeneous absorbent polymer compositions with similar capacities. Without being bound by theory, it is believed that the increase in modulus of the surface layer affords increased resistance to deformation under an applied load, and hence increased porosity and permeability. The gradation in crosslinking from surface to interior can vary, both in depth and profile.

A number of processes for introducing surface crosslinks are disclosed in the art. Suitable methods for surface crosslinking include those where (i) a di- or poly-functional reagent(s) capable of reacting with existing functional groups within the absorbent polymer is applied to the surface of the absorbent polymer; (ii) a di- or poly-functional reagent that is capable of reacting with other added reagents and possibly existing functional groups within the absorbent polymer such as to increase the level of crosslinking at the surface is applied to the surface (e.g., the addition of monomer plus crosslinker and the initiation of a second polymerization reaction); (iii) no additional polyfunctional reagents are added, but additional reaction(s) is induced amongst existing components within the absorbent polymer either during or after the primary polymerization process such as to generate a higher level of crosslinking at or near the surface (e.g., suspension polymerization processes wherein the crosslinker is inherently present at higher levels near the surface); and (iv) other materials are added to the surface such as to induce a higher level of crosslinking or otherwise reduce the surface deformability of the resultant swollen polymer.

Suitable general methods for carrying out surface crosslinking of absorbent polymers according to the present invention are disclosed in U.S. Patent 4,541,871 (Obayashi), issued September 17, 1985; published PCT application WO92/16565 (Stanley), published October 1, 1992, published PCT application WO90/08789 (Tai), published August 9, 1990; published PCT application WO93/05080 (Stanley), published March 18, 1993; U.S. Patent 4,824,901 (Alexander), issued April 25, 1989; U.S. Patent

4,789,861 (Johnson), issued January 17, 1989; U.S. Patent 4,587,308 (Makita), issued May 6, 1986; U.S. Patent 4,734,478 (Tsubakimoto), issued March 29, 1988; U.S. Patent 5,164,459 (Kimura et al.), issued November 17, 1992; published German patent application 4,020,780 (Dahmen), published August 29, 1991; and published European
5 patent application 509,708 (Gartner), published October 21, 1992; all of which are incorporated herein by reference. For cationic absorbent polymers, suitable di- or poly-functional crosslinking reagents include di/poly-haloalkanes, di/poly-epoxides, di/poly-acid chlorides, di/poly-tosyl alkanes, di/poly-aldehydes, di/poly-acids, and the like.

In addition to surface crosslinking, several other approaches have been utilized to
10 improve the permeability, and/or the absorption rate of the absorbent. For example, U.S. Patent 5,419,956 (Roe), issued on May 30, 1995, describes the addition of inorganic particles such as silica to superabsorbent polymers to improve fluid uptake rate and to increase fluid distribution. Japanese patent application JP 11-012,367 (Kajikawa et al),
15 published on January 19, 1999, that discloses manufacturing of superabsorbent polymers with high liquid permeability and high absorption rate by adding fine powders to the corresponding superabsorbent polymers. GB-A-2.082.614 (Richman) describes the addition (either under wet or dry conditions) of between 1 and 75% of an extender material such as cellulose derivatives, or inorganic materials like clay or minerals. The objective of this development is an increase of absorbent capacity.

20 A further known approach for improving the liquid handling performance of absorbent polymers is the addition of inorganic material during the formation of the polymer or the cross-linking thereof, which can be used to reduce gel blocking. An approach along these lines is described in US-A-4.500.670 (McKinley), wherein structures are described which have between 1 and 99% of an inorganic powder added,
25 which provides an increase of gel strength from less than about 0.1 psi to 2.1 psi (at 40 % inorganic powder). Such gel strengths are typically characteristic of materials exhibiting SFC values below $60 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ and such high amounts of inorganic powder will also reduce the overall absorbent capacity of the mixture.

Also in US-A-4.578.308 (Makita) addition of an inert inorganic powder before the drying
30 step of the polymer manufacturing process is described, so as to incorporate this inert material into aggregates formed during the drying.

Absorbent polymer particles can be substantially affected during processing in the manufacture of absorbent articles. Abrasion of the surface and/or breaking of the individual particles tends to occur, resulting in the generation of smaller particles.

Without being bound by theory, it is believed that the relatively small particles produced during the damaging process tend to fill the voids between the larger particles, thereby reducing the permeability of the system. Furthermore, in surface-crosslinked materials, it is believed that damage to the polymer particles exposes the inner material which has a relatively low degree of crosslinking. In the swollen state, this inner material has relatively low gel strength, and tends to deform to fill residual void spaces within the gel bed. Thus, damage to the absorbent polymer particles can substantially reduce the permeability of the material and/or the rate of fluid absorption. This reduction in the rate of absorption is typically undesirable in absorbent products such as diapers, which contain such absorbent polymers. This reduction in the rate of absorption is even more undesired in the typical designs of absorbent articles and structures of today, which exhibit relatively high concentrations of absorbent polymer in the absorbent structure, as the risk of gel blocking becomes more pronounced at higher concentration of absorbent polymer. The effects of damage are further pronounced in modern designs and methods to create such designs, whereby greater amounts of absorbent material are preferably applied in shorter times, thus representing harsher processing conditions as seen by the materials.

Although there have been many efforts directed towards improving the liquid permeability and/or the absorption rate of absorbent polymers prior to damaging, including the addition of inorganic particles, these efforts have not been directed towards improving the permeability of absorbent polymers after damaging.

Accordingly, it would be desirable to devise a process which would attenuate the reduction in permeability typically observed upon damage to absorbent polymers caused during the typical manufacturing processes for disposable absorbent articles.

It would further be desirable if such process for maintaining permeability were compatible with existing processes for manufacturing absorbent polymer compositions and/or absorbent products, as well as being facile and inexpensive.

SUMMARY OF THE INVENTION

The present invention is a process of making an absorbent structure wherein absorbent polymer particles, which having an SFC value of more than $5 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$, are mixed with a Permeability Maintenance Agent, preferably a particulate one, and then combined with a carrier, which can be fibrous, or a porous web, such as a fibrous web or a foam.

During the combination step a mechanical stress is applied to the polymer particles, whereby the effect of this mechanical stress on the permeability should be less for the blend of the polymer particles with the Permeability Maintenance Agent, compared to the effect of the mechanical stress on an analogous material without the Permeability Maintenance Agent. Preferably, the effect of reduction in SFC values for the absorbent polymer particles without addition of the Permeability Maintenance Agent is at least $5 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater, preferably at least $10 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater, and even more preferably at least $20 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater than the reduction in SFC for the absorbent polymer particle/Permeability Maintenance Agent blend.

Preferably, the absorbent polymer particles material exhibits an SFC value of at least $20 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$, more preferably of at least $40 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$, and even more preferably more than $60 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$. The absorbent polymer particles can have a particle size distribution such that at least 30% by weight has a particle size of more than $300 \mu\text{m}$. Preferred Permeability Maintenance Agents are silica, preferably fumed silica. The Permeability Maintenance Agent can have an average particle size of no more than $10 \mu\text{m}$, preferably no more than $1 \mu\text{m}$ or even less than $0.1 \mu\text{m}$. The Permeability Maintenance Agent can be added at a level of not more than 3.0%, preferably not more than 1.0 %, and more preferably of not more than 0.8%, and even more preferably of not more than 0.6% based on the total weight of said absorbent polymer particles, and said Permeability Maintenance Agent, and at a level of at least 0.2%, preferably more than 0.4%.

The process can include the step of transporting and or storing said absorbent polymer particles/Permeability Maintenance Agent blend prior to or after said mixing step. The mixing step can be dry mixing of dry absorbent polymer particles and dry Permeability Maintenance Agent. The combination step can be dry mixing of the absorbent polymer particles/Permeability Maintenance Agent blend with a carrier, such as an airlaying process.

The absorbent structure made according to the present invention preferably comprises at least 40%, more preferably at least 60%, even more preferably at least 80% absorbent polymer particles, and most preferably more than 90 % based on the total weight of said absorbent polymer particles, said carrier, and said Permeability Maintenance Agent.

The present invention also relates to an absorbent structure comprising a absorbent polymer particles/Permeability Maintenance Agent blend having an SFC reduction in a damaging test of less than 10% relative to the SFC of the AAP without Permeability Maintenance Agent prior to damaging.

DETAILED DESCRIPTION OF THE INVENTION

A. Definitions

As used herein, the term "body fluids" includes urine, blood, menses and vaginal discharges.

As used herein, the term "synthetic urine solution" refers to an aqueous solution prepared by dissolving 2.0 g KCl, 2.0 g Na₂SO₄, 0.85 g NH₄H₂PO₄, 0.15 g (NH₄)₂HPO₄, 0.25 g CaCl₂·2H₂O, and 0.50 g MgCl₂·6H₂O in distilled water to yield one liter of solution.

As used herein, the term "absorbent polymer" refers to a polymer which has a Gel Volume (GV) of at least 10 g/g.

As used herein, the term "damaging test" refers to one of the two damaging protocols specified in the "Examples" section

As used herein, the term "absorbent core" refers to the component of the absorbent article that is primarily responsible for fluid handling properties of the article, including acquiring, transporting, distributing and storing body fluids. As such, the absorbent core typically does not include the topsheet or backsheet of the absorbent article.

As used herein, the term "absorbent member" refers to the components of the absorbent core that typically provide one or more fluid handling properties, e.g., fluid acquisition, fluid distribution, fluid transportation, fluid storage, etc. The absorbent member can comprise the entire absorbent core or only a portion of the absorbent core, i.e., the absorbent core can comprise one or more absorbent members. The improved absorbent polymer compositions described herein are particularly useful in absorbent members whose primary function is the storage of aqueous body fluids. However, these compositions may also be present in other absorbent members.

As used herein, the term "comprising" means various components, members, steps and the like can be conjointly employed according to the present invention. Accordingly, the term "comprising" encompasses the more restrictive terms "consisting

essentially of" and "consisting of," these latter, more restrictive terms having their standard meaning as understood in the art.

All percentages, ratios and proportions used herein are by weight unless otherwise specified.

5 All publications and references referred to herein are incorporated by reference, at least to the extent they are consistent with the terms and definitions of the present disclosure.

B. Absorbent Polymers

10 The present invention relates, to a process of making absorbent structures wherein absorbent polymer compositions are used, and in particular compositions that exhibit high absorbency of synthetic urine solution under an applied load as well as high permeability to fluid in the swollen state, after the polymer composition has been exposed to mechanical stress such as during the manufacturing process of the absorbent structure. The absorbent polymer compositions include a variety of water-insoluble, but
15 water-swallowable polymers. These are typically lightly crosslinked polymers which contain a multiplicity of acid functional groups such as carboxylic acid groups. Examples of acid polymers suitable for use herein include those which are prepared from polymerizable, acid-containing monomers, or monomers containing functional groups which can be converted to acid groups after polymerization. Thus, such monomers include olefinically
20 unsaturated carboxylic acids and anhydrides, and mixtures thereof. The acid polymers can also comprise polymers that are not prepared from olefinically unsaturated monomers.

Examples of such polymers include polysaccharide-based polymers such as carboxymethyl starch and carboxymethyl cellulose, and poly(amino acid) based
25 polymers such as poly(aspartic acid). For a description of poly(amino acid) absorbent polymers, see, for example, U.S. Patent 5,247,068, issued September 21, 1993 to Donachy et al., which is incorporated herein by reference.

Some non-acid monomers can also be included, usually in minor amounts, in preparing the absorbent polymers herein. Such non-acid monomers can include, for
30 example, monomers containing the following types of functional groups: carboxylate or sulfonate esters, hydroxyl groups, amide-groups, amino groups, nitrile groups, quaternary ammonium salt groups, and aryl groups (e.g., phenyl groups, such as those derived from styrene monomer). Other optional non-acid monomers include unsaturated hydrocarbons such as ethylene, propylene, 1-butene, butadiene, and isoprene. These

non-acid monomers are well-known materials and are described in greater detail, for example, in U.S. Patent 4,076,663 (Masuda et al.), issued February 28, 1978, and in U.S. Patent 4,062,817 (Westerman), issued December 13, 1977, both of which are incorporated herein by reference.

5 Olefinically unsaturated carboxylic acid and anhydride monomers include the acrylic acids typified by acrylic acid itself, methacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -stearylacrylic acid, itaconic acid, citroconic acid, mesaconic acid, 10 glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, and maleic anhydride.

Preferred absorbent polymers contain carboxyl groups. These polymers include hydrolyzed starch-acrylonitrile graft copolymers, partially neutralized hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, partially neutralized 15 starch-acrylic acid graft copolymers, hydrolyzed vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile or acrylamide copolymers, slightly network crosslinked polymers of any of the foregoing copolymers, polyacrylic acid, and slightly network crosslinked polymers of polyacrylic acid. These polymers can be used either solely or in the form of a mixture of two or more different polymers. Examples of these polymer materials are 20 disclosed in U.S. Patent 3,661,875, U.S. Patent 4,076,663, U.S. Patent 4,093,776, U.S. Patent 4,666,983, and U.S. Patent 4,734,478.

Most preferred polymer materials for use in making the absorbent polymers are slightly network crosslinked polymers partially neutralized polyacrylic acids and starch derivatives thereof.

25 Most preferably, the absorbent polymers comprise from about 50-95, preferably about 75% neutralized, slightly network crosslinked, polyacrylic acid (i.e., poly (sodium acrylate/acrylic acid)). Network crosslinking renders the polymer substantially water-insoluble and, in part, determines the absorptive capacity and extractable polymer content characteristics of the absorbent polymers. Processes for network crosslinking 30 these polymers and typical network crosslinking agents are described in greater detail in U.S. Patent 4,076,663.

While the absorbent polymer is preferably of one type (i.e., homogeneous), mixtures of absorbent polymers can also be used in the present invention. For example, mixtures of starch-acrylic acid graft copolymers and slightly network crosslinked 35 polymers of polyacrylic acid can be used in the present invention.

In absorbent structures as made according to the present invention, there can be used one and the same polymer type or composition throughout the total structure, or there can be different types or compositions in different parts of the structure. A material or composition can have the same concentration throughout the structure, or can be at
5 varying concentrations distributed therethrough.

For the absorbent polymers according to the present invention, the particle size and particle size distribution - such as can be determined by conventional sieving or optical methods - is of lesser importance. In contrast to the materials disclosed in US-A-5.419.956 (Roe et al), wherein the absorbent polymer is required to have a particularly
10 narrow particle size distribution, and to have less than about 30% of the material of a particle size of more than about 300 μm , the present invention is not limited by this constraint. Even further, in order to enhance the permeability properties, it can be advantageous to have more than 30% of the particles having a particle size of more than about 300 μm . For the purposes of this invention, particle size distributions are
15 determined according to the method described in the Test Methods section of US-A-5.419.956 (Roe et al).

C. Methods for Making Absorbent Polymers

The absorbent polymers useful in the present invention can be formed by any polymerization and/or crosslinking techniques. Typical processes for producing these
20 polymers are described in U.S. Reissue Patent 32,649 (Brandt et al.), issued April 19, 1988, U.S. Patent 4,666,983 (Tsubakimoto et al.), issued May 19, 1987, and U.S. Patent 4,625,001 (Tsubakimoto et al.), issued November 25, 1986, all of which are incorporated by reference.

Polymerization methods to prepare absorbent polymers useful in the present
25 invention can include free radical, ring-opening, condensation, anionic, cationic, or irradiation techniques. The polymer may be prepared in the neutralized, partially neutralized, or un-neutralized form, even though the desired product is un-neutralized. The absorbent polymer may be prepared using a homogeneous solution polymerization process, or by multi-phase polymerization techniques such as inverse emulsion or
30 suspension polymerization procedures.

Crosslinking can be effected during polymerization by incorporation of suitable crosslinking monomers. Alternatively, the polymers can be crosslinked after polymerization by reaction with a suitable reactive crosslinking agents. Surface crosslinking of the initially formed polymers is a preferred process for obtaining absorbent

polymers having relatively high PUP capacity, porosity and permeability. Without being bound by theory, it is believed that surface crosslinking increases the resistance to deformation of the surfaces of swollen absorbent polymer particles, thus reducing the degree of contact between neighboring polymer particles when the swollen particles are deformed under an external pressure. Surface crosslinked absorbent polymers have a higher level of crosslinking in the vicinity of the surface than in the interior. As used herein, "surface" describes the outer-facing boundaries of the particle. For porous absorbent polymers (e.g., porous particles, etc.), exposed internal boundaries can also be included. By a higher level of crosslinking at the surface, it is meant that the level of functional crosslinks for the absorbent polymer in the vicinity of the surface is generally higher than the level of functional crosslinks for the polymer in the interior. The gradation in crosslinking from surface to interior can vary, both in depth and profile.

A number of processes for introducing surface crosslinks are disclosed in the art. Suitable methods for surface crosslinking include those where (i) a di- or poly-functional reagent(s) capable of reacting with existing functional groups within the absorbent polymer is applied to the surface of the absorbent polymer; (ii) a di- or poly-functional reagent that is capable of reacting with other added reagents and possibly existing functional groups within the absorbent polymer such as to increase the level of crosslinking at the surface is applied to the surface (e.g., the addition of monomer plus crosslinker and the initiation of a second polymerization reaction); (iii) no additional polyfunctional reagents are added, but additional reaction(s) is induced amongst existing components within the absorbent polymer either during or after the primary polymerization process such as to generate a higher level of crosslinking at or near the surface (e.g., suspension polymerization processes wherein the crosslinker is inherently present at higher levels near the surface); and (iv) other materials are added to the surface such as to induce a higher level of crosslinking or otherwise reduce the surface deformability of the resultant hydrogel. Suitable general methods for carrying out surface crosslinking of absorbent polymers according to the present invention are disclosed in U.S. Patent 4,541,871 (Obayashi), issued September 17, 1985; published PCT application WO92/16565 (Stanley), published October 1, 1992; published PCT application WO90/08789 (Tai), published August 9, 1990; published PCT application WO93/05080 (Stanley), published March 18, 1993; U.S. Patent 4,824,901 (Alexander), issued April 25, 1989; U.S. Patent 4,789,861 (Johnson), issued January 17, 1989; U.S. Patent 4,587,308 (Makita), issued May 6, 1986; U.S. Patent 4,734,478 (Tsubakimoto), issued March 29, 1988; U.S. Patent 5,164,459 (Kimura et al.), issued November 17,

1992; published German patent application 4,020,780 (Dahmen), published August 29, 1991; and published European patent application 509,708 (Gartner), published October 21, 1992; all of which are incorporated herein by reference.

5 D. Permeability Maintenance Agent

An essential element for processes according to the present invention is an agent which is added to the absorbent polymers to allow that such materials experience a smaller decrease in permeability upon exposure to mechanical stress than do analogous materials without such agent.

10 In particular, modern processes aim at producing absorbent structures with high ratios of absorbent polymers relative to the carrier means - concentrations of 60% of absorbent polymer in a matrix of 40% fibrous materials are not unusual any more. At the same time, such processes aim at producing at higher and higher production speeds.

Such usage rate increases are often achieved by using conventional equipment -
15 such as for transporting, metering or positioning of the material - which originally was designed for much lower usage rates, often 50%, or even 20% of the rates currently employed. A conventional approach is to increase the flow rates of the material - or the transport speed or velocity - through the system. Often, this results in increase of the mechanical stress which is exerted on the materials due to increased abrasion, collision
20 with walls, etc..

The current invention uses an additive to the absorbent polymer in order to reduce their susceptibility of the absorbent polymer to a reduction in performance caused by mechanical stress, in particular with regard to the permeability of such materials, as evaluated by the "Saline Flow Conductivity" (SFC). Such an additive is referred to herein
25 as a Permeability Maintenance Agent.

An essential element for the present invention is the addition of a particulate material to the absorbent polymer. Any fine powder may be used as such a particulate material, such as - without any limitation - silica, silicon dioxide, amorphous silica, alumina, titanium dioxide, clays, or other non-absorbent polymer particles, such as can
30 be produced by grinding, emulsion polymerization, precipitation polymerization techniques, or any combination of the foregoing materials. The size of the particulate material can be determined by conventional particle size analysis methods, such as sieving or optical analysis, and is typically no more than 10 μm , and often less than about 1.0 μm or even less than 0.1 μm . Preferably, the powder used herein comprises fine

amorphous fumed silica, such as that in the form of a product referred to as Cab-O-Sil L-90, manufactured by Cabot Corporation, Tuscola, IL.

The fine powder may be added in concentrations up to about 3%, preferably not more than 1.0%, more preferably not more than 0.8%, and most preferably not more than 0.6 %, whilst at least 0.2%, preferably 0.4% should be added, all percentages being based on the total mixture of absorbent polymer and fine powder.

E. Blending or Mixing

The process of the current invention includes mixing or blending the fine powder with the absorbent polymer particles so as to achieve a homogeneous blend of the two materials. The materials may be blended or mixed in the dry state, or in the form of a slurry or suspension. Preferably, the materials are blended in the dry state. Whilst a number of conventional methods can be applied, preferred blending processes aim for a homogeneous distribution of the materials.

The blending process should further be as gentle as possible so as to minimize the extent of abrasion and/or breakage of the absorbent polymer particles. Mixing may be done in a continuous process, or in a batchwise fashion.

Preferred suitable equipment for such a gentle process is generally known to one skilled in the art, such as ploughshare mixer as available from Gebr. Lödige Maschinebau GmbH, Germany, under the designation KM as continuous mixer, or FM as batch mixer, or as continuous mixer from Schugi BV, Netherlands, or as batch mixer from H.Forberg, Norway.

F. Method of making absorbent structures

Methods of forming absorbent structures wherein particulate absorbent materials is held in a fixed position by means of a carrier are well known in the art. Generally, the absorbent structure should be porous to allow liquid transport, and the carrier should be a fibrous material or a porous substrate, such as a fibrous or foam web. The polymer material can then be added to this carrier, and can be mechanically trapped by the carrier, such as is the case with conventional cellulose batts comprising fluff and particulate absorbent materials, or with a porous web enveloping the materials. The polymer material can be attached to the carrier by an attachment means, such as adhesives, or chemical agents, which can bond the particles to the substrate, either

permanently, such as by covalent chemical bonding, or temporarily which refers in this context to a bonding mechanism, such as hydrogen bonding, which loses its bond strength upon wetting, such as during use.

When the fixation is achieved by containing the particulate material between
5 layers of such a carrier, these can be bonded to each other such as by the above referred adhesives or covalent bonding means, or by compression, or crimping, preferably in a particular pattern so as to create pockets with the particulate absorbent material therein.

When the carrier comprises fibers, these can be natural, preferably cellulosic
10 fibers, or man-made fibers, such as viscose/rayon fibers, or synthetic polymer fibers, which can comprise polyethylene, polypropylene, polyester or polyamine, which can be made of pure monomers, or can be co-polymers. Also, Bi- or multi-component fibers can be used. Such fibers can be individualized, such as when using fluff pulp, or can be pre-formed into a web, such as tissues, or non-woven, or woven materials.

Also, foamed structures, or apertured films can be used as a carrier, provided
15 these have appropriate liquid handling properties, especially an adequate permeability.

A preferred execution for the present invention relates to combining cellulose fluff
fibers with particulate absorbent polymer and Permeability Maintenance Agent blend,
such as disclosed and described in US-A-5.017.324 (Kaiser); US-A-4.770.344 (Kaiser);
20 EP-A-0.439.012 (Pieper); US-A-5.494.622 (Heath); EP-A0.292.623 (Angstadt); US-A-
4.755.178 (Insley); US-A-5.879.751 (Bogdanski), US-A-4.927.582 (Bryson); all of which
are incorporated herein by reference.

For all these processes, the absorbent material is acquired in large quantities
from the material supplier, and is then transported to the production line of the absorbent
25 article, where it is metered into the absorbent structures there formed. From an economic
point of view, it is often desirable to have the means for the transport to the lines and on
the lines with minimal dimensions for the respective throughput. Often, particulate
absorbent is fed through a piping system, with an air pressure differential as driving
means. In such systems, the mechanical stress on the material can be significant, such
30 as by interaction with walls of the transporting means or control member (like valves, or
metering units), but also by interaction between the particles themselves. In particular at
high transport rates, the resulting average particle speed can reach significant values.
This mechanical stress can have negative impact on the performance properties of the
material as discussed separately in more detail

G. Effect of Permeability Maintenance Agent

It is a particular effect of the Permeability Maintenance Agent to minimize this negative effect of the mechanical stress on the physical characteristics of the material, especially on the permeability of the material, such as expressed by the Saline Flow Conductivity (SFC). It should be noted, that the addition of the Permeability Maintenance Agent increase the SFC of the material even before it is subjected to significant mechanical stress, which can be an increase of the SFC values. However, this effect needs to be separated from the effect of minimizing the reduction of the SFC value during the mechanical stress inducing process.

Without wishing to be bound by theory, it is believed, that the Permeability Maintenance Agent reduces the friction between the particles and either walls or other particles, and thus actually minimizes the damaging stress for the particles, which otherwise could result in break-up of the particle, or - especially for materials which have a particular surface cross-linked shell - damage or abrasion of this treated shell, and hence reduced efficiency.

H. Physical Properties

(i) Performance Under Pressure (PUP)

Measurement of the Demand Wettability or Gravimetric Absorbence can provide information on the ability of a high concentration zone or layer of the absorbent polymer to absorb body fluids under usage pressures. See, for example, U.S. Patent 5,562,646 (Goldman et al.) issued October 8, 1996 and U.S. Patent 5,599,335 (Goldman et al.) issued Feb. 4, 1997 where Demand Wettability or Gravimetric Absorbence is referred to as Performance Under Pressure (PUP).

(ii) Permeability of the Zone or Layer Comprising Absorbent Polymer

As indicated above, a requisite property of absorbent polymers of the present invention is their relatively high permeability to fluid. In an absorbent member or article, this directly affects the ability of a material, such as a layer comprising swollen absorbent polymer, to transport body fluids away from the acquisition region at an acceptable rate. Permeability/flow conductivity can be defined in terms of Saline Flow Conductivity (SFC), which is a measure of the ability of a material to transport saline fluid.

For the purposes of the present invention, an absorbent polymer is deemed to have requisite permeability properties if its SFC value is at least about $50 \times 10^{-7} \text{ cm}^3$

sec/g. A method for measuring saline flow conductivity is described in U.S. Patent 5,562,646 (Goldman et al.) issued October 8, 1996.

I. Test Methods

1. Performance Under Pressure (PUP) Capacity

5 This test is described in U.S. Patent 5,599,335 (Goldman et al.) issued Feb. 4, 1997. The test determines the amount of synthetic urine solution absorbed by absorbent polymers that are laterally confined in a piston/cylinder assembly under a confining pressure of 0.7 psi.

Saline Flow Conductivity (SFC)

10 A measure of permeability and an indication of porosity is provided by the saline flow conductivity of the gel bed as described in U.S. Patent No. 5,562,646, (Goldman et al.) issued Oct. 8, 1996.

Gel Volume Determination (GV)

15 This test is described in U.S. Patent 4,654,039 (Brandt et al.) issued Mar. 31, 1987. The test determines the amount of synthetic urine solution imbibed by absorbent polymers that are in contact with the solution.

J. Specific Examples

Example 1

(i) Absorbent Polymer Control

20 A lightly crosslinked, partially-neutralized poly(acrylic acid) absorbent polymer with a relatively high PUP capacity (~27 g/g at 0.7 psi; 60 minutes) is obtained from Chemdal Corp., Palatine, Illinois (ASAP-400; lot no. 38121A0203). (Similar samples of ASAP-400 are available from The Procter & Gamble Co., Paper Technology Division, Cincinnati, OH.) This material is designated as Sample 1.

25 ii) Damaging

Approximately 10 grams of the absorbent polymer composition (Sample 1) are placed in an 8 oz blending jar designed to be used with an Osterizer blender (Model # 855-08K). The mixture is blended on low speed at approximately 1200 rpm for 1 minute to complete damaging of the absorbent polymer (Sample 1D).

30 (iii) Preparation of Absorbent Polymer/Silica Blend

To prepare the absorbent polymer/silica blend, 10 grams of absorbent polymer (Sample 1) are weighed into a 25 ml (8 dram) glass vial with external dimensions of approximately 9.5 cm in height x 2.5 cm diameter (available from VWR. Co., West Chester, PA; Catalog No. 66011-165). About 0.0601 grams Cab-O-Sil L-90, Lot # 1J193,

Cabot Corporation) are added to the absorbent polymer and mixed thoroughly using a Vortex Mixer (manufactured by Scientific industries Inc., Bohemia, NY; Model No. G-560; available from VWR. Co., West Chester, PA) or equivalent mixer, for approximately 1 minute (Sample 1S).

5 (iv) Damaging

Approximately 10 grams of the absorbent polymer composition (Sample 1S) are placed in an 8 oz blending jar designed to be used with an Osterizer blender (Model # 855-08K). The mixture is blended on low speed at approximately 1200 rpm for 1 minute to complete damaging of the absorbent polymer/silica blend (Sample 1SD).

10 (v) Capacity Measurements (PUP)

PUP capacities are measured as described in the Test Methods section of U.S. Patent 5,599,335. Approximately 0.9 grams of the unsieved damaged absorbent polymer composition are transferred to a PUP cylinder, and gently spread out over the entire area of the screen comprising the base of the cylinder. The PUP capacity is
15 determined under a confining pressure of 0.7 psi with the amount of fluid absorbed measured at frequent intervals for a period of 1 hour. Selected PUP capacity data are listed in Table 1 below.

 (vi) Permeability Measurement (SFC)

Saline Flow Conductivity is measured as described in the Test Methods section of
20 U.S. Patent 5,562,646. Approximately 0.9 grams of the absorbent polymer composition are transferred to a cylinder designed for Saline Flow Conductivity measurement cylinder, and gently spread out over the entire area of the screen comprising the base of the cylinder. The measured saline flow conductivity values are listed in Table 1 below:

Table 1:

25 PUP Capacities and SFC Values for Absorbent Polymer Compositions

| | PUP | SFC |
|----------------------------|--------|-----|
| Undamaged Control Sample 1 | 27 g/g | 82 |
| Damaged Control Sample 1D | 25 g/g | 32 |
| Damaged Blend Sample 1SD | 24 g/g | 185 |

SFC values are $\times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

A comparison of the SFC values indicates that the permeability of the damaged absorbent polymer - silica blend (Sample 1SD) is substantially greater than that of the damaged control sample without silica (Sample 1D) under analogous test conditions.

5 A comparison of the PUP capacities indicates that damaged absorbent polymer - silica blend (Sample 1SD) has approximately the same PUP capacity as the damaged control sample (Sample 1D)

Example 2

(i) Preparation of Absorbent Polymer/Silica Blend

10 To prepare the absorbent polymer/silica blend, about 10 grams of absorbent polymer (Sample 1 from Example 1) are weighed into a 25 ml (8 dram) glass vial with external dimensions of approximately 9.5 cm in height x 2.5 cm diameter (available from VWR. Co., West Chester, PA; Catalog No. 66011-165). About 0.05 g Sipernat D-17 (hydrophobic precipitated silica, Degussa Corporation, Ridgefield Park, NJ) are added to the absorbent polymer and mixed thoroughly using a Vortex Mixer (manufactured by
15 Scientific industries Inc., Bohemia, NY; Model No. G-560; available from VWR. Co., West Chester, PA) or equivalent mixer, for approximately 1 minute (Sample 2S).

(ii) Damaging

20 Approximately 10 grams of the absorbent polymer composition (Sample 2S) are placed in an 8 oz blending jar designed to be used with an Osterizer blender (Model # 855-08K). The mixture is blended on low speed at approximately 1200 rpm for 1 minute to complete damaging of the absorbent polymer/silica blend (Sample 2SD).

(iii) PUP Capacity Measurements

25 PUP capacities are measured as described in the Test Methods section of U.S. Patent 5,599,335. Approximately 0.9 grams of the unsieved damaged absorbent polymer composition are transferred to a PUP cylinder, and gently spread out over the entire area of the screen comprising the base of the cylinder. PUP capacities are determined under confining pressures of 0.7 with the amount of fluid absorbed measured at frequent intervals for a period of 1 hour. PUP capacity data are listed in Table 2 below.

(iv) Permeability Measurement

30 Saline Flow Conductivity is measured as described in U.S. Patent No. 5,562,646. Approximately 0.9 grams of the unsieved absorbent polymer composition are transferred to a cylinder designed for Saline Flow Conductivity measurement (SFC), and gently

spread out over the entire area of the screen comprising the base of the cylinder. The measured saline flow conductivity values are listed in Table 2 below:

Table 2:

PUP Capacities and SFC for Absorbent Polymer Compositions

| | PUP | SFC |
|----------------------------|--------|-----|
| Undamaged Control Sample 1 | 27 g/g | 82 |
| Damaged Control Sample 1D | 25 g/g | 32 |
| Damaged Blend Sample 2SD | 27 g/g | 122 |

SFC values are $\times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

A comparison of the SFC values indicates that the permeability of the absorbent polymer - silica blend (Sample 2SD) is substantially greater than that of the damaged control sample (Sample 1D) under the analogous test conditions.

A comparison of the PUP capacities indicates that the damaged absorbent polymer - silica blend (Sample 2SD) has a similar PUP capacity to the damaged absorbent polymer control (Sample 1D) under the test conditions described.

Example 3

(i) Preparation of Absorbent Polymer/Silica Blend

To prepare the absorbent polymer/silica blend, 490 grams of absorbent polymer (Sample 1 from Example 1) are weighed into a ceramic Mill Jar with external dimensions of approximately 14.6 cm in diameter \times 17 cm height (U.S. Stoneware, available from VWR. Co., West Chester, PA; Catalog No. 48906-029). About 2.45 grams Cab-O-Sil L-90 amorphous fumed silica (Lot # 1J193, Cabot Corporation, Tuscola, IL) are added to the absorbent polymer in the Mill Jar and the jar is securely capped. The absorbent polymer-silica blend is thoroughly mixed by rotating the Mill Jar using a roller type Jar Mill (U.S. Stoneware, available from VWR. Co., West Chester, PA; Catalog No. 48900-000) at 90 rpm for 4.5 hours (Sample 3S).

(ii) Damaging

Approximately 10 grams of the absorbent polymer composition (Sample 3S) are placed in an 8 oz blending jar designed to be used with an Osterizer blender (Model # 855-08K). The mixture is blended on low speed at approximately 1200 rpm for 1 minute to complete damaging of the absorbent polymer/silica blend (Sample 3SD).

(iii) PUP Capacity Measurements

PUP capacities are measured as described in the Test Methods section of U.S. Patent 5,599,335. Approximately 0.9 grams of the unsieved damaged absorbent polymer composition are transferred to a PUP cylinder and gently spread out over the entire area of the screen comprising the base of the cylinder. The PUP capacity is determined under a confining pressure of 0.7 psi with the amount of fluid absorbed measured at frequent intervals for a period of 1 hour. Selected PUP capacity data are listed in Table 3 below.

(iv) Permeability Measurement

Saline Flow Conductivity is measured as described in U.S. Patent No. 5,562,646. Approximately 0.9 grams of the absorbent polymer composition are transferred to a cylinder designed for Saline Flow Conductivity measurement (SFC), and gently spread out over the entire area of the screen comprising the base of the cylinder. The measured SFC values are listed in Table 3 below:

Table 3:

PUP Capacities and SFC for Absorbent Polymer Compositions

| | PUP | SFC |
|----------------------------|--------|-----|
| Undamaged Control Sample 1 | 27 g/g | 82 |
| Damaged Control Sample 1D | 25 g/g | 32 |
| Damaged Blend Sample 3SD | 27 g/g | 144 |

SFC values are $\times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

A comparison of the SFC values indicates that the permeability of the damaged absorbent polymer - silica blend (Sample 3SD) is substantially greater than that of the damaged control sample without silica (Sample 1D) under analogous test conditions.

A comparison of the PUP capacities indicates that the damaged absorbent polymer - silica blend (Sample 3SD) has slightly higher PUP capacity than the damaged absorbent polymer control (Sample 1D) under the test conditions described.

Example 4

(i) Preparation of Absorbent Polymer/Silica Blend

To prepare the absorbent polymer - silica blend, 25.0 grams of absorbent polymer (Sample 1 from Example 1) are weighed into a 150 ml glass beaker with an internal

diameter of approximately 52 mm. A mechanical stirrer equipped with a 10 mm glass shaft and 48 mm polytetrafluoroethylene blade (Ace Glass Inc., Louisville, KY; catalog Nos. 8070-05 and 8085-03) is set up to stir the absorbent polymer with the flat side of the blade across the bottom of the beaker. About 1.43 grams of colloidal silica (35% solids, MA-ST colloidal silica in methanol, Nissan Chemical Industry, lot number 70673) and 1.5 grams of distilled water are thoroughly mixed in a 1 dram glass vial. The silica suspension is then added dropwise to the absorbent polymer over a period of about 30 seconds while the mixture is stirred at approximately 170 rpm, to yield an absorbent polymer-silica agglomerate. The agglomerate is mixed gently with spatula to ensure uniform mixing and is dried in a vented oven at 65°C for 1 hour (Sample 4S).

(ii) Damaging

Approximately 20 grams of absorbent polymer composition (Sample 4S) are placed into a Mill Jar with external dimensions of approximately 14.6 cm in diameter × 17 cm height (U.S. Stoneware, available from VWR. Co., West Chester, PA; Catalog No. 48906-029) equipped with 12 Burundum cylinders (U.S. Stoneware, available from VWR. Co., West Chester, PA; Catalog No. 48908-024). The securely capped Mill Jar is rotated on a roller type Jar Mill (U.S. Stoneware, available from VWR. Co., West Chester, PA; Catalog No. 48900-000) at approximately 60 rpm for 5 minutes (Sample 4SD).

(iii) PUP Capacity Measurements

PUP capacities are measured as described in the Test Methods section of U.S. Patent 5,599,335. Approximately 0.9 grams of the unsieved absorbent polymer composition are transferred to a PUP cylinder and gently spread out over the entire area of the screen comprising the base of the cylinder. The PUP capacity is determined under a confining pressure of 0.7 psi with the amount of fluid absorbed measured at frequent intervals for a period of 1 hour. Selected PUP capacity data are listed in Table 4 below.

(iv) Permeability Measurement

Saline Flow Conductivity is measured as described in U.S. Patent No. 5,562,646. Approximately 0.9 grams of the unsieved absorbent polymer composition are transferred to a cylinder designed for Saline Flow Conductivity measurement, and gently spread out over the entire area of the screen comprising the base of the cylinder. The measured saline flow conductivity values are listed in Table 4 below:

Table 4:

PUP Capacities and SFC for Absorbent Polymer Compositions

| | PUP | SFC |
|----------------------------|--------|-----|
| Undamaged Control Sample 1 | 27 g/g | 82 |
| Damaged Control Sample 1D | 25 g/g | 32 |
| Damaged Blend Sample 4SD | 26 g/g | 74 |

SFC values are $\times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

5 A comparison of the SFC values indicates that the permeability of the damaged absorbent polymer - silica blend (Sample 4SD) is substantially greater than that of the damaged control sample without silica (Sample 1D) under the analogous test conditions.

A comparison of the PUP capacities indicates that the damaged absorbent polymer - silica blend (Sample 4SD) has a similar PUP capacity to the damaged absorbent polymer control (Sample 1D) under the test conditions described.

10 Example 5 The following example demonstrates the effect of the addition of silica on permeability of absorbent polymer prior to versus after being exposed to mechanical stress or damaging.

(i) Damaging

15 Approximately 5 grams of the absorbent polymer composition (Sample 1 from Example 1) are placed in an 8 oz blending jar designed to be used with an Osterizer blender (Model # 855-08K). The absorbent polymer is damaged on low speed at approximately 1200 rpm for 1 minute to yield the damaged absorbent polymer Sample 5D.

(ii) Preparation of Damaged Absorbent Polymer/Silica Blend

20 To prepare the damaged absorbent polymer/silica blend, about 5 grams of damaged absorbent polymer (Sample 5D) are weighed into a 25 mL (8 dram) glass vial with external dimensions of approximately 9.5 cm in height \times 2.5 cm diameter (available from VWR. Co., West Chester, PA; Catalog No. 66011-165). About 0.025 grams Sipernat D-17 (hydrophobic precipitated silica, Degussa Corporation, Ridgefield Park, NJ) are added to the absorbent polymer and mixed thoroughly using a Vortex Mixer
25 (manufactured by Scientific industries Inc., Bohemia, NY; Model No. G-560; available from VWR. Co., West Chester, PA) or equivalent mixer, for approximately 1 minute (Sample 5SD).

(iii) PUP Capacity Measurements

PUP capacities are measured as described in the Test Methods section of U.S. Patent 5,599,335. Approximately 0.9 grams of the unsieved damaged absorbent polymer composition are transferred to a PUP cylinder, and gently spread out over the entire area of the screen comprising the base of the cylinder. PUP capacities are determined under confining pressures of 0.7 with the amount of fluid absorbed measured at frequent intervals for a period of 1 hour. PUP capacity data are listed in Table 5 below.

(iv) Permeability Measurement

Saline Flow Conductivity is measured as described in U.S. Patent No. 5,562,646. Approximately 0.9 grams of the unsieved absorbent polymer composition are transferred to a cylinder designed for Saline Flow Conductivity measurement (SFC), and gently spread out over the entire area of the screen comprising the base of the cylinder. The measured saline flow conductivity values are listed in Table 5 below:

Table 5:

PUP Capacities and SFC for Absorbent Polymer Compositions

| | PUP | SFC |
|---------------------------|--------|-----|
| Damaged Control Sample 1D | 25 g/g | 32 |
| Damaged Blend Sample 2SD | 27 g/g | 122 |
| Damaged Blend Sample 5SD | 24 g/g | 69 |

SFC values are $\times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$.

A comparison of the SFC values indicates that the permeability of the absorbent polymer - silica blend (Sample 2SD) whereas the silica is added prior to damaging is substantially greater than that of the polymer - silica blend (Sample 5SD) where the silica is added after damaging under the analogous test conditions.

A comparison of the PUP capacities indicates that the damaged absorbent polymer - silica blend (Sample 5SD) has a similar PUP capacity to the damaged absorbent polymer control (Sample 1D) under the test conditions described.

Claims:

1. A process of making an absorbent structure comprising the steps of providing
- 5 absorbent polymer particles having an SFC value of more than $5 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$,
- a carrier,
 - a Permeability Maintenance Agent
 - a mixing means for mixing said absorbent polymer particles with said Permeability Maintenance Agent,
 - 10 - a combining means for forming an absorbent structure comprising said absorbent polymer particles and said carrier;
- mixing said absorbent polymer particles with said Permeability Maintenance Agent using said mixing means to form an absorbent polymer particle/Permeability Maintenance Agent blend;
- 15 combining said absorbent polymer particle/Permeability Maintenance Agent blend with said carrier using said combining means to form said absorbent structure, whereby a mechanical stress is applied to said absorbent polymer particle/Permeability Maintenance Agent blend by the interaction of said absorbent polymer particle/Permeability Maintenance Agent blend and said combining means.
- 20 2. A process for making an absorbent structure according to claim 1, wherein said mechanical stress reduces the SFC value of said absorbent polymer particle/Permeability Maintenance Agent blend, whereby the reduction in SFC is less for the absorbent polymer particle/Permeability Maintenance Agent blend than for the absorbent polymer particles without Permeability Maintenance Agent.
- 25 3. A process for making an absorbent structure according to claim 2, wherein said reduction in SFC for said absorbent polymer particles without addition of said Permeability Maintenance Agent is at least $5 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater, preferably at least $10 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater, and even more preferably at least $20 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$ greater than the reduction in SFC for said absorbent polymer
- 30 particle/Permeability Maintenance Agent blend.

4. A process for making an absorbent structure according to any of the preceding claims, wherein said absorbent polymer particles exhibit an SFC value of at least $20 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$, preferably of at least $40 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$, and even more preferably of at least $60 \times 10^{-7} \text{ cm}^3 \cdot \text{sec/g}$
- 5 5. A process for making an absorbent structure according to any of the preceding claims, wherein at least 30% by weight of said absorbent polymer particles has a particle size of more than 300 μm .
6. A process of making an absorbent structure according any of the preceding claims, wherein said Permeability Maintenance Agent is a particulate material.
- 10 7. A process of making an absorbent structure according to any of the preceding claims, wherein said Permeability Maintenance Agent is silica, preferably fumed silica.
8. A process of making an absorbent structure according to any of claims 1 to 3, wherein said Permeability Maintenance Agent has an average particle size of no
15 more than 10 μm , preferably no more than 1 μm or even less than 0.1 μm .
9. A process of making an absorbent structure according to any of the preceding claims, wherein said Permeability Maintenance Agent is added at a level of not more than 3.0%, preferably not more than 1.0 %, and more preferably of not more than 0.8%, and even more preferably of not more than 0.6% based on the total
20 weight of said absorbent polymer particles, and said Permeability Maintenance Agent.
10. A process of making an absorbent structure according to any of the preceding claims, wherein said Permeability Maintenance Agent is added at a level of at least 0.2%, preferably more than 0.4%, based on the total weight of said absorbent
25 polymer particles, and said Permeability Maintenance Agent.
11. A process of making an absorbent structure according to any of the preceding claims, further comprising the step of transporting and or storing said absorbent polymer particle/Permeability Maintenance Agent blend prior to or after said combination step.

12. A process of making an absorbent structure according to any of the preceding claims, wherein said absorbent polymer particles and said Permeability Maintenance Agent are essentially dry, wherein said combining step is dry mixing.
- 5 13. A process of making an absorbent structure according to any of the preceding claims, wherein said carrier comprises fibers.
14. A process of making an absorbent structure according to claim 13, wherein said combination of said fibers with said absorbent polymer particle/Permeability Maintenance Agent blend is achieved by mixing.
- 10 15. A process of making an absorbent structure according to any of the preceding claims, wherein said carrier comprises a porous structure, preferably a foam or a fibrous web.
16. A process of making an absorbent structure according to claim 15, wherein said absorbent polymer particles are positioned in contact with said porous structure, and affixed thereto.
- 15 17. A process of making an absorbent structure according to any of the preceding claims, wherein said structure comprises at least 40%, preferably at least 60%, most preferably at least 80% absorbent polymer particles, and even more preferably more than 90 % based on the total weight of said absorbent polymer particles, said carrier, and said Permeability Maintenance Agent.
- 20 18. An absorbent structure obtainable by a process according to any of the preceding claims, characterized in that said structure comprises an absorbent polymer particle/Permeability Maintenance Agent blend having an SFC reduction in a damaging test of less than 10% relative to the SFC of the absorbent polymer particles without Permeability Maintenance Agent prior to damaging.

25

INTERNATIONAL SEARCH REPORT

International Application No:
PCT/US 00/05724

A. CLASSIFICATION OF SUBJECT MATTER
A61F13/15

According to International Patent Classification (IPC) or to both national classification and IPC⁷

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|----------------------------|
| A | US 5419956 A (ROE) 30 May 1995, column 5, lines 13-45, column 10, lines 1-44, column 11, line 9 - column 12, line 12, claims. (cited in the application) -- | 1, 6- 10, 12, 13, 19 |
| A | US 4500670 A (McKINLEY et al.) 19 February 1985, column 1, line 61 - column 2, line 17, column 2, line 55 - column 3, line 49, claims. (cited in the application) -- | 1, 6, 12 |
| A | US 4286082 A (TSUBAKIMOTO et al.) | 1, 6- 10, 12 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search
06 November 2000

Date of mailing of the international search report
1 5. 12. 00

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INTERNATIONAL SEARCH REPORT

PCT/US 00/05724

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| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p>25 August 1981, column 6, lines 38-66, column 7, line 65 - column 8, line 33, table 1,2, example 4, claims. --</p> <p>WO 97/12575 A1 (THE PROCTER & GAMBLE COMPANY) 10 April 1997, page 5, line 9-14, page 9, lines 25-27, page 13, lines 1-16, claims. ----</p> | <p>1, 5, 13-15</p> |

| ANHANG | | ANNEX | | ANNEXE | |
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| Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr. | | To the International Search Report to the international Patent Application No. | | Au rapport de recherche international relatif à la demande de brevet international n° | |
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| In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr. | | This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. | | La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l' Office. | |
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